

Recent Development of Rechargeable Lithium-ion Cells at JPL

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ABSTRACT

The objective of this work is to identify electrode materials and electrolytes for lithium-ion cells to be used in NASA's **New Millennium** spacecraft and to demonstrate the advantage of this technology. Recent progress has shown that the electrode fabrication method plays an important role. The test performance of cells containing these electrodes has led to the selection of graphite anode material, LiCoO_2 cathode material, Celgard 2500 separator, and 1 M LiPF_6 in (30% EC + 70% DMC) electrolyte as our base line Li-ion cell materials. In addition, the evaluation of new alternative non-carbon type anode material in Li-ion cells is also discussed. We also applied the Taguchi design method to assist in the identification of key cell design parameters. All of the above factors mentioned, as well as the development of low temperature Li-ion cell systems, are discussed below.

Introduction

Lithium-ion technology has emerged as a viable alternative to the use of lithium metal in rechargeable cells⁽¹⁾. This technology represents a new generation of safe, lightweight, and high energy rechargeable batteries. It is also attractive due to the capability of long cycle life combined with an energy density that exceeds all long lived aqueous rechargeable batteries. Our work has focused on designing and building "proof-of-concept" cells of small size (550 mAh to 3 Ah) with LiCoO_2 positive and graphite negative electrodes. Specifically, the research has involved the study of new anode materials, effect of different types of electrolytes, types of separators, electrode fabrication techniques, Taguchi cell design studies, selection of carbon (coke or graphite) materials, and development of low temperature rechargeable Li-ion cells. The Li-ion cell chemistry in our present configuration offers promise for future spacecraft applications. In this paper, we summarized the results of our recent studies on Li-ion cell development

evaluated. The positive electrode, using aluminum foil as substrate, was made from a mixture of LiCoO_2 , Shawinigan black and PVdF binder. Microporous polypropylene, either Celgard 2400 or 2500, was used as the separator material. The electrolyte used for cells containing either graphite carbon or Mg_2Si anode was 1 M LiPF_6 in mixed (by volume ratio) solvents containing ethylene carbonate (EC) and carbonates (e.g. dimethyl carbonate (DMC), diethyl carbonate (DEC)). However, the electrolyte used for cells having coke anodes was 1 M LiPF_6 in propylene carbonate (PC) and dimethoxyethane (DME). The electrolytes were stored under lithium chips for at least one week prior to use. Experimental spirally wound sealed cells were constructed for performance evaluation. All of the cell assembly operations were carried out in an oxygen and moisture free glovebox. The test cells were evaluated for charge and discharge characteristics, faradaic utilization of the electrode active materials, rate capability and cycle life. The test cells were discharged at constant current. Two methods (either constant current or constant voltage) were used for the charging of the test cells.

Experimental

The anode materials used in this study were either carbon (coke or graphite) or non-carbon type (Mg_2Si) materials. The anode active materials (carbon or Mg_2Si) was mixed with polyvinylidene fluoride (PVdF) binder in the appropriate solvent to produce a slurry and spray-coated on copper foil substrates. In addition, Mg_2Si anodes were made with a Teflon (TFE) binder in the same manner and were also

Results and Discussion

(1) **Electrode Fabrication Method:** In addition to some previously in-house developed electrode fabrication techniques (dipping, painting and pressing), a spray-coated method was developed to prepare the cathodes and anodes on 1 mil thick aluminum and copper foil substrates, respectively. PVdF material was used as the electrode binder

and its composition was 6 wt. % in the electrodes. The average thickness of the anodes is 10 mil and is about half the thickness of those electrodes made with a painting method on a grid-type substrate. From our experimental test results, the combined effect of thin electrodes and uniform loading increased the carbon anode utilization from 180 mAh/g to 220 mAh/gm.

(2) **Effect of Separator Type:** Two types of separators (Celgard 2400 and 2500) have been evaluated in the full cell configuration. Both separators are 1 mil in thickness. Celgard 2500 has a higher porosity than that of Celgard 2400. Upon dipping the two separators into the 1M LiPF₆ in (30% EC + 70% DMC) electrolyte, it was observed that Celgard 2500 showed a better wetting ability towards the electrolyte. The test results of cells containing different separators indicated that the utilizable lithium capacity of the anode material in cells using Celgard 2500 separator increased substantially at the C/3 discharge rate. However, the irreversible Li capacity per gram of anode active material is about the same. The performance comparison of anode active material in cells using the Celgard 2400 or 2500 separators is shown in Table I.

Table I. Evaluation of Separators

Type Of Separator	Celgard 2400	Celgard 2500
Material	Microporous	Microporous
Thickness	1 mil	1 mil
Discharge Rate	90%	90%
Wetability to Elyte	Good	Very Good
Rev. Cap. (mAh/g)	152 - 201	240 - 260
Irrrev. Cap. (mAh/g)	55 - 60	55 - 60

(3) **Evaluation of Carbon Anode Materials:** Several graphite (KS-15 and KS-44 graphite from Lionza, Osaka carbon, and JPL graphite) and coke (Conoco, Mitsubishi) materials were evaluated in full cells containing 1M LiPF₆ in (30% EC + 70% DMC) or 1M LiPF₆ in (50% EC + 50% DMC) electrolyte, respectively. The results indicate that the coke materials evaluated showed a reversible Li capacity of 150 ~ 170 mAh/g and an irreversible Li capacity of 140 ~ 150 mAh/g. The graphite materials can deliver a reversible Li capacity of ~250 mAh/g and an irreversible Li capacity of 60 ~ 90 mAh/g. The test results of various carbon anode materials are compared in Table II.

Table II. Evaluation of Carbon Anode Materials

Carbon Type	Rev.Cap.(mAh/g)	Irrrev.Cap.(mAh/g)
Conoco Coke	150	153
Mitsubishi Coke	170	139

Osaka Carbon	250	70
JPL Graphite	250	60
KS-15 Graphite	252	62
KS-44 Graphite	252	92

(4) **Effect of Electrolytes on Anode Performance:** The result of previous electrolyte studies⁽²⁻⁴⁾ have shown that the carbon anode performance is dependent significantly on the electrolyte type (salts and solvents) and composition (volume percentage of EC or PC). Recent studies on four electrolytes (1M LiPF₆ in 33% EC + 33% DEC + 34% DMC, 1M LiPF₆ in 30% EC + 70% DEC, 1M LiPF₆ in 30% EC + 70% DMC, and 1M LiPF₆ in 50% EC + 50% DMC) indicated that the JPL graphite/LiCoO₂ Li-ion cells activated with the first three electrolytes can deliver comparable reversible Li capacities (~250 mAh/g) and irreversible Li capacities (~60 mAh/g). Whereas, the cells containing 1M LiPF₆ in 50% EC + 50% DMC electrolyte yields a lower reversible Li capacity (~148 mAh/g) and a large irreversible Li capacity (~113 mAh/g). The experimental results of Li-ion cells containing various electrolytes are summarized in Table III.

Table III. Evaluation of Electrolytes

Electrolytes	Rev.Cap.(mAh/g)	Irrrev.Cap.(mAh/g)
30/70 EC-DMC	250	60
50/50 EC-DMC	148	112
33/33/34 EC-DEC-DMC	253	58
30/70 EC-DEC	240	50

(5) **Evaluation of New Anode Materials:** Carbon materials (such as graphite, coke, pitch and PAN fibers) are currently being evaluated in lithium batteries as alternative anode materials⁽¹⁾. Some degree of success has been achieved. However, the effort to look for other non-carbon anode materials which have larger Li capacity, higher rate capability, smaller first charge capacity loss and better mechanical stability during cycling is continuing. One possibility is magnesium silicide (Mg₂Si). It is evident from the Mg-Si binary phase diagram that Mg₂Si is the only compound formed between Mg and Si⁽⁵⁾. The compound Mg₂Si has a fluorite structure, which is face-centered cubic, with Si atoms at the cube corners and face centers, and Mg atoms occupying all the tetrahedral sites. This material was studied as an anode material at 400 °C using a molten salt electrolyte⁽⁶⁾. The proposed Li-Mg-Si ternary phase diagram⁽⁷⁾ at 400 °C shows that intercalation of Li into Mg₂Si will form the Mg and Li₁₃Si₄ phases. However, the electrochemical and thermodynamic properties of Li₁₃Mg₂Si at room temperature was not studied. Thus, the feasibility of using Li₁₃Mg₂Si as an alternate anode material

at ambient temperature in organic electrolyte cell is not known. Recently, we have tried to intercalate Li into this material electrochemically at room temperature using an organic electrolyte. A voltage plateau at 260 mV (vs Li) was observed, which is very attractive for using this material as an alternate anode. The Li de-intercalation out of $\text{Li}_x\text{Mg}_2\text{Si}$ was also evaluated and the result is shown in Figure 1.

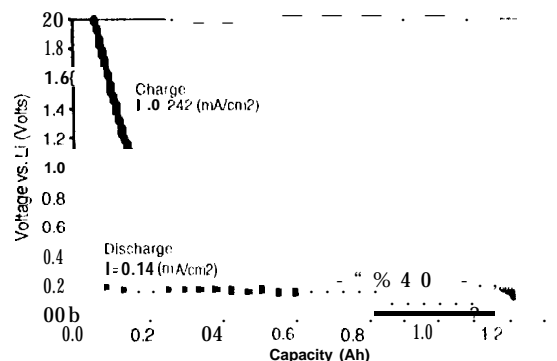


Figure 1. Charge and discharge profiles for the Li/EC/DMC/ Mg_2Si cell.

X-ray diffraction (XRD) analysis revealed that it is possible to electrochemically intercalate about one Li per Mg_2Si while still retaining the crystal structure. The XRD results did not show evidence for the existence of the Mg or Li_2Si phases. The ambient temperature electrochemical intercalation of Li into Mg_2Si forms single phase(s) instead of multi-phases. Continued Li intercalation beyond the composition $\text{Li}_{1.0}\text{Mg}_2\text{Si}$ caused the material to become amorphous. Experimental $\text{Mg}_2\text{Si}/\text{LiCoO}_2$ cells, containing an electrolyte of 1.0M LiPF_6 in EC + DMC, were fabricated and the electrical performance of these cells was evaluated. The charge and discharge profiles of the cells are shown in Figure 2. Experimental results and observations indicate that the Mg_2Si electrode integrity was good and stable in the non-aqueous organic electrolyte. These experimental cells have completed 70 cycles (Figure 3).

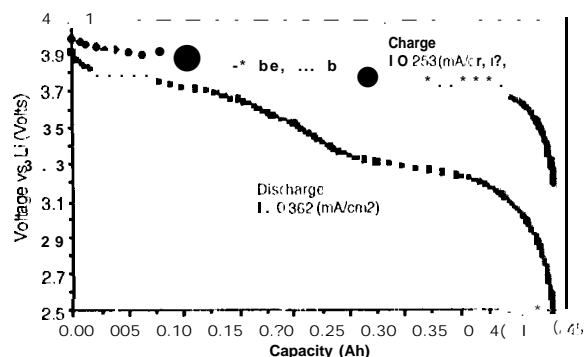


Figure 2. Charge and discharge profiles for the $\text{Mg}_2\text{Si}/\text{EC/DMC}/\text{LiCoO}_2$ cell.

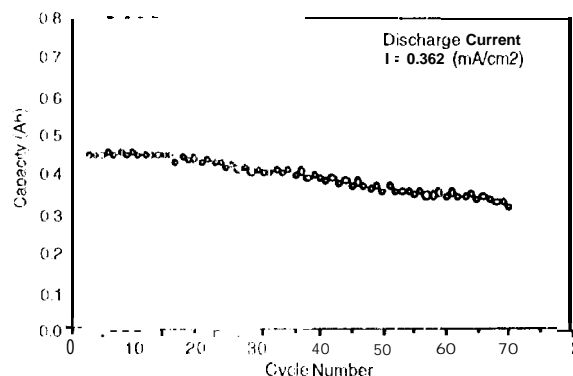


Figure 3. Cycle life performance of $\text{Mg}_2\text{Si}/\text{LiCoO}_2$ cell.

(6) Li-ion Cell Design Study: A task was initiated to investigate the influence of key design parameters on Li-ion cell performance using a robust design approach (Taguchi method). This experimental design approach has several advantages, including the option of evaluating more than one variable at a time as well as the benefit of being able to reduce the number of experiments that need to be studied. It also helps the study of the interaction between design parameters. Under a contract from JPL, Wilson Greatbatch LTD. (WGL) applied Taguchi methods to assess the effects of design factors on Li-ion cell (using coke anode) performance. In the study, a matrix of L_8 orthogonal array was chosen for the evaluation of seven design factors at two levels. The seven factors investigated include: (1) cathode materials, (2) anode materials, (3) electrode porosity, (4) interelectrode spacing, (5) cell balance, (6) electrolyte salt, and (7) electrolyte solvent type. It was found that the major factors which control the cell performance are: cell balance, electrolyte salt type, electrolyte solvent type, and type of Carbon. Based on the summary of the work, several cells will be fabricated and tested to confirm the feasibility of this design approach.

(7) Low Temperature Li-ion Cell Study: Various rechargeable battery systems, such as Ni/Cd or Ni/H, have attractive specific and power densities but limited operating temperature range due to the use of aqueous-based electrolyte in most cases. In addition, the realizable efficiencies and energy densities of these systems are rather low at subzero temperatures. The ambient temperature of some of NASA's planetary missions are much lower than -20°C . This necessitates insulation of the battery from extreme ambient temperatures prevalent at planetary surfaces and possibly a warm up of the battery by another energy source. No electrochemical systems are known to function effectively in such cold environments. At JPL, we propose to carry out studies leading to an identification and evaluation of such a cryogenic battery system, based on our present understanding of the advanced Li and Li-ion battery systems. The limited temperature range of the existing battery systems is due to

the freezing of the electrolyte solution at temperatures below -20°C . Accordingly, the proposed study begins with a series of experiments leading to an identification of suitable electrolyte solutions based on solvents that maintain an liquid state at low temperature. The goal of the electrolyte sub-task is to identify an electrolyte with a conductivity of 10^{-4} to 10^{-3} S/cm in the temperature range of 40 to 0°C . The specific objective of the electrode material sub-task is to identify high specific energy electrode materials with fast lithium ion diffusivity at low temperatures.

Summary

The recent progress of our Li-ion cell development has been described in this paper. A spray-coated method was developed to fabricate electrodes with uniform load and predictable performance. The test results of the electrical performance of cells containing these electrodes and different types of separators leads to the selection of Celgard 2500 as a promising separator for Li-ion cells. In addition, we have identified a new candidate Li-ion cell chemistry based on the Mg_2Si anode. However, the detailed microstructure and phase changes still need further investigation. By using the Taguchi analysis, it has been determined that the cell performance is highly dependent on the key parameters, such as the electrode capacity ratio, types of electrolyte and types of carbon. A cryogenic Li-ion cell system based on advanced low temperature electrolytes and electrode materials is currently under development for extreme environmental application.

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References

- (1) T. Nagaura, Denchi Gijutsu, 3 (1991) 100.
- (2) "Evaluation of Carbon Anodes for Rechargeable Lithium Cells", C.-K. Huang, S. Surampudi, A. Attia and G. Halpert, Proceedings of the 182nd Meeting of Electrochem. Soc., Toronto, Canada, Oct. (1992).
- (3) "Effect of Electrolyte Composition on Carbon Electrode Performance", C.-K. Huang, S. Surampudi, D. H. Shen and G. Halpert, Proceedings of the 184th Meeting of Electrochem. Soc., New Orleans, Louisiana, Oct. (1993).
- (4) "Development of Ambient Temperature Lithium-ion Cells", C.-K. Huang, B. V. Ratnakumar, S. Surampudi, and G. Halpert, Proceedings of the 186th Meeting of Electrochem. Soc., Miami Beach, Florida, Oct. (1994).
- (5) E. Peled, J. Golodnitsky, G. Ardel, C. Menachem, D. Bar-Tow and V. Eslikenazy, Proceedings of Materials Research Society Meeting, San Francisco, CA., Apr. 17-21, 1995.
- (6) Thaddeus B. Massalski, etc., Binary Alloy Phase Diagrams, 2nd Edition Volume 3, P. 2547.
- (7) R. A. Huggins & A. Anani, U. S. Patent # 4,950,566.